The evolution of a W, Au-Ag-Te and Au-Ag hydrothermal system, Tinos Island, Cyclades, Greece

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Abstract

At Tinos Island, Greece, the physicochemical evolution of the hydrothermal system and the associated stages of metallic mineralization that are developed in the vicinity of the Tinos granodiorite-leucogranite has been studied, based on fluid inclusion studies and chemical reactions modeling. Early tungsten mineraliozation was related to the metasomatic stage of contact metamorphism and precipitated at ~ 350oC, from moderate saline (10.4 to 14.8 wt% NaCl eq.), CO2- effervescing fluids, that contained variable amounts of CaCl2 and MgCl2. Panormos Bay Au-Ag-Te mineralization, located 16 km away from the intrusive site, was deposited from cooler 200° to 300oC, and low to moderate saline (0.2 to 13.2 wt% NaCl eq.) mineralizing fluids. Au-Ag mineralization at Apigania Bay, which represents a late evolutionary phase, was deposited from even cooler (125o to 235oC) and dilute (0.2 to 6.8 wt % NaCl eq.) fluids. In all, the mineralization stage precipitation was controlled by two principal factors: the exsolution of gaseous phase and an increase in pH from 3.3 to 7.6.

Keywords

Tungsten, Gold-silver-tellurium, Gold-silver-bearing mineralization, Skarn, Panormos Bay, Apigania Bay, Tinos, Greece

Disciplines

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Comments

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ABSTRACT: At Tinos Island, Greece, the physicochemical evolution of the hydrothermal system and the associated stages of metallic mineralization that are developed in the vicinity of the Tinos granodiorite-leucogranite has been studied, based on fluid inclusion studies and chemical reactions modeling. Early tungsten mineralization was related to the metasomatic stage of contact metamorphism and precipitated at ~ 350°C, from moderate saline (10.4 to 14.8 wt% NaCl eq.), CO_2-effervescing fluids, that contained variable amounts of $CaCl_2$ and $MgCl_2$. Panormos Bay Au-Ag-Te mineralization, located 16 km away from the intrusive site, was deposited from cooler 200° to 300°C, and low to moderate saline (0.2 to 13.2 wt% NaCl eq.) mineralizing fluids. Au-Ag mineralization at Apigania Bay, which represents a late evolutionary phase, was deposited from even cooler (125° to 235°C) and dilute (0.2 to 6.8 wt % NaCl eq.) fluids. In all, the mineralization stage precipitation was controlled by two principal factors: the exsolution of gaseous phase and an increase in pH from 3.3 to 7.6

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1 INTRODUCTION

Unexploited tungsten-molybdenum mineralization occurs within the contact aureole of the syntectonic calc-alkaline Tinos intrusion, and may be genetically related to gold-silver telluride mineralization at Panormos Bay, and gold-silver mineralization at Apigania Bay, Tinos Island, Greece. In this study, detailed investigations of paragenetic and fluid inclusions characteristics have been conducted to constrain the evolution and provenance of the mineralizing fluids at the three localities.

2 GEOLOGICAL SETTING

The tectonic stratigraphy at Tinos consists of a series of stacked nappes cut by a Miocene pluton (Melidonis, 1980). The lowest of these nappes, the Basal Unit, consists of a platform of late Triassic to late Cretaceous neritic carbonate rocks. This unit is overlain by the Intermediate nappe or Blueschist Unit, a package of tholeiitic mafic to felsic volcanic rocks and associated metasediments metamorphosed to blueschist facies (40-50 Ma), and subsequently retrograded to greenschist facies (*ca.* ~ 25 Ma) (Andriessen *et al.*, 1987). Overlying this are the klippen of the Upper Unit, which represent ancient oceanic crust metamorphosed to greenschist facies that was emplaced at ~ 18 Ma (Andriessen *et al.*, 1987). The Tinos pluton was intruded syntectonically, and displays thermal-tectonic contacts with the Blueschist and Upper Units (Mastrakas, 2007).

3 TINOS PLUTONIC ROCKS, CONTACT AUREOLE AND SKARNS

The Miocene Tinos pluton consists of a central body of I-type biotite-hornblende granodiorite that was emplaced at *ca.* 17 Ma (Altherr *et al.*, 1982) under compression (Mastrakas and St. Seymour, 2000). An S-type leucogranite with the assemblage biotite-muscovite-garnet-tourmaline was emplaced peripherally to the granodiorite, and also as sills at shallow levels in an extensional regime (Mastrakas & St. Seymour, 2000). The age of emplacement of the leucogranite has been determined as *ca.* 14 Ma (K-Ar ages, Altherr *et al.*, 1982). The genesis of the granodiorite magma is attributed to partial melting of mafic lower crustal rocks, whereas the leucogranite melt with melt contribution from the granodiorite represents a hybrid partial melt consisting mainly of metasedimentary country rock. Geobarothermometric studies indicate that the granodiorite was emplaced at a temperature range of 750° to 800°C and at pressures of ~ 4.7 kbars, whereas the leucogranite was emplaced *ca.* 680°C and at ~ 2 kbars (Mastrakas, 2007). The latter experienced intense retrograde boiling as evidenced by numerous miarolitic cavities. The Tinos pluton caused contact metamorphism at *ca.* 14 Ma (Bröcker *et al.*, 1993). A discontinuous scapolite zone is surrounded successively by pyroxene-, hornblende-, albite- and epidote-hornfels zones (Mastrakas, 2007).

Skarn rocks are developed within amphibolite schists and marbles of the Blueschist Unit, and outcrop as podiform, lensoid and vein-like bodies and mainly as an exoskarn near marble-amphibolite schist contacts. In general, skarns are spatially related to leucogranite apophyses and aplitic stockworks. Skarns consist predominantly of garnet and clinopyroxene. Hornblende replaced clinopyroxene and grew in open spaces with calcite, quartz, feldspar, titanite and epidote. Accessory minerals include apatite, tourmaline, allanite and wollastonite, locally, in the marbles. Application of the pyroxene-garnet geothermometer of Pattison & Newton (1989) to pyroxene-garnet skarn rocks gave non-equilibrium results, with frequency peaks occurring at 680°, 550°C (attributed to an early contact metamorphic thermal-isochemical stage); and a number of values between 375° and 320° C (related to a late infiltration metasomatism event, which occurred at pressures of < 500bars; Mastrakas, 2007).

4 ORES ASSOCIATED WITH THE TINOS PLUTON

4.1. Scheelite Mineralization

Tungsten mineralization is hosted in skarns and hornfelses. Scheelite occurs as disseminations and mainly as massive aggregates in discontinuous zones, up to 30 cm wide, subparallel to the schistosity, particularly in silicified-carbonatized zones or as residual crusts on fractures. Scheelite mineralization, which makes up to 20 vol. % of the skarn, occurs in garnet-pyroxene skarns (grossular-rich grandite coexisting with hedenbergite during the contact metamorphic episode evolved to andratite-rich oscillatory zoned garnet coexisting with salite-diopside) containing magnetite, chalcopyrite, pyrrhotite, pyrite and lesser sphalerite. Open spaces in the skarn are locally filled with calcite, apatite, hornblende, chlorite, titanite, quartz, feldspar, molybdenite and scheelite. Scheelite deposition was likely controlled by the reaction:

$$CaCO_{3(s)} + H_2WO_4{}^0{}_{(aq)} = CaWO_{4(s)} + H_2O_{(l)} + CO_{2(g)} \quad (1)$$

4.2. Panormos Bay mineralized vein system

The Panormos Bay mineralized vein system is hosted in marbles of the Basal and Blueschist Units and consists of 30 subparallel steeply dipping banded, syntaxial stockworks of quartz veins. Marble units are intruded by two generations of veins, an older, northeasterly-trending set of milky quartz veins and a younger group of northwesterly trending clear quartz veins.

Alteration haloes formed as concentric shells and planar bodies that envelope milky and clear quartz veins. Blueschist Unit marbles develop assemblages composed of muscovite, albite and tourmaline, whereas alteration haloes in dolomitic marbles of the Basal unit consist of two successive zones: an inner *talc zone* and an outer *chlorite zone*. Talc zones are characterized by an assemblage of milky quartz, talc, calcite, brucite, muscovite, and albite. Chlorite zones consist of major clear and minor milky quartz, chlorite, epidote, muscovite, albite and barite. Formation of talc-brucite-calcite is interpreted to have been controlled by the reaction:

$$CaMg(CO_3)_{2(s)} + 4SiO_{2(aq)} + 2Mg^{+2} + 3H_2O_{(l)} = Mg_3Si_4O_{10}(OH)_{2(s)} + CaCO_{3(s)} + CO_{2(g)} + 4H^+$$

(2)

Seventy metallic and gangue minerals, including Cu-cervelleite and an unnamed Ag-Au-Cu sulphotelluride were identified. Eight paragenetic stages of hypogene mineralization with the assemblages: pyrite, arsenopyrite, pyrrhotite (Stage I); tetrahedrite, tennantite, goldfieldite (Stage II); bornite, chalcopyrite (Stage III); Sn sulphides, sulphosalts of As and Sb and arsenides of Ni or Co (Stage IV); tellurides (Stage V); galena, betekhtinite, argentite (Stage VI); wurtzite, greenockite, smithsonite (Stage VII); native gold, silver, copper, arsenic, stromeyerite, pyrargyrite (Stage VIII) were followed by supergene mineralization (stage IX) (Tombros *et al.*, 2004, 2005). Precipitation of Ag-, and Au- tellurides was likely associated with reactions (3) and (4), whereas native precious metals were deposited by reactions (5) and (6):

$$2Ag(HS)^-_2 + HTe^-_{(aq)} = 4HS^-_{(aq)} + Ag_2Te_{(s)} + H^+_{(aq)} \quad (3)$$

$$Au(HS)^-_{2(aq)} + 2HTe^-_{(aq)} + 0.75O_{2(g)} + H^+_{(aq)} = 2HS^-_{(aq)} + AuTe_{2(s)} + 1.5H_2O_{(l)} \quad (4)$$

$$0.5H_2O_{(l)} + Au(HS)^-_{2(aq)} = Au_{(s)} + 2HS^-_{(aq)} + H^+_{(aq)} + 0.25O_{2(g)} \quad (5)$$

$$Ag(HS)^-_{2(aq)} + 0.5H_2O_{(l)} = Ag_{(s)} + H^+_{(aq)} + 2HS^-_{(aq)} + 0.25O_{2(g)} \quad (6)$$

4.3. Apigania Bay mineralized vein system

The Apigania Bay vein system is hosted in marbles, blueschists, greenschists, amphibolites and ultramafics of the Blueschist Unit (Tombros, 2001); and consists of five high-angle quartz veins, which bear considerable resemblance to veins at Panormos Bay. Alteration haloes comprise an inner *epidote zone* and an outer *chlorite zone*. The epidote zone is associated with milky quartz, albite, muscovite and ankerite, whereas the chlorite zone contains clear and minor milky quartz, chlorite, calcite, albite and muscovite.

There are three paragenetic stages of hypogene mineralization: pyrite, sphalerite, pyrrhotite, arsenopyrite, magnetite, argentite, electrum, stephanite, xanthoconite, proustite, canfieldite (Stage I); tetrahedrite, famatinite, chalcopyrite, rammelsbergite, laggisite, cassiterite (Stage II); and galena, argentite-acanthite, polybasite, electrum, argentopyrite (Stage III). A supergene stage (Stage IV) follows the hypogene stages (Tombros & St. Seymour, 1998). Electrum precipitation in Stages I and III was controlled by reaction (7):

$$0.5H_2O_{(l)} + 0.7Au(HS)^-_{2(aq)} + 0.3Ag(HS)^-_{2(aq)} = Au_{0.7}Ag_{0.3(s)} + 2HS^-_{(aq)} + H^+_{(aq)} + 0.25O_{2(g)} \quad (7)$$

5 FLUID INCLUSION STUDIES

Microthermometric measurements were made in the Laboratory of High Temperature Processes at the Department of Earth and Planetary Sciences of McGill University. Temperatures were measured with an alumel-chromel thermocouple, and the readings were calibrated with synthetic inclusions. Measurements are accurate to within ± 1°C. Microthermometric data were reduced using the FLINCOR software (Brown, 1989).

At room temperature, fluid inclusions were classified into three types based on the number and proportion of phases: (i) L-V inclusions predominate, and consist of aqueous liquid + vapor (< 25 vol. %). They contain no solids, whereas formation of gas hydrates was observed during freezing and these homogenize to liquid upon heating, (ii) V-L inclusions with irregular shapes and consisting of aqueous liquid + vapour (up to 80 vol. %). The V-L inclusions are primary, infrequently observed and homogenize to the vapor phase upon heating, and (iii) L-L-V inclusions consist of aqueous liquid + carbon dioxide liquid + vapor. Formation of gas hydrates was observed in some of the L-L-V inclusions during freezing.

L-L-V primary fluid inclusions (~5 % of inclusion population) occur in milky quartz veinlets cross cutting garnet cores from the skarn, and in milky quartz and calcite from Panormos Bay. V-L primary inclusions occur in scheelite and milky quartz veinlets, smoky and milky quartz and calcite from Panormos Bay mineralization. L-V primary, pseudosecondary and secondary inclusions are located in all three mineralizations.

The temperatures of last melting of ice ($T_{m\text{-}ice}$) and clathrates ($T_{m\text{-}clathrate}$) of the L-V, V-L and L-L-V inclusions, in scheelite and associated milky quartz vary from -10.4° to -10.2°C and 0.7° to 5.7°C, respectively. These values correspond to salinities of 10.4 to 14.8 wt% NaCl equivalent, using the equations of Brown & Lamb (1989) and Darling (1991). The homogenization temperatures (T_h) of these inclusions vary from 315° to 400 °C. The $T_{m\text{-}ice}$ and $T_{m\text{-}clathrate}$ values for fluid inclusions in smoky quartz range from -6.6° to -5.7°C and 6.7° to 7.7°C, respectively, corresponding to salinities of 4.5 to 6.8 wt% NaCl equivalent, whereas the T_h values range from 281° to 320°C.

At Panormos Bay, the $T_{m\text{-}ice}$ and $T_{m\text{-}clathrate}$ values of fluid inclusions in milky vein and clear quartz range from -4.4° to -2.3°C, 7.7° to 8.5°C, and -4.1° to -2.0°C, 8.8° to 9.6°C corresponding to salinities of 1.1 to 7.9 and 0.8 to 5.6 wt% NaCl equivalent. The T_h values of inclusions range from 245° to 292°C and 198° to 253°C, respectively. At Apigania Bay the $T_{m\text{-}ice}$ values of fluid inclusions in milky vein and clear quartz range from -4.3° to -0.4°C, and -3.6° to -0.1°C, respectively, corresponding to salinities of 3.0 to 6.8 and 0.2 to 5.5 wt% NaCl equivalent. The T_h values range from 173° to 235°C and 125° to 168°C, respectively.

6 DISCUSSION

Based on results derived from reactions 1 to 7, it is likely that precipitated the mineralizations ore deposition on Tinos Island were controlled by pH, CO_2-effervescence, depletion of H_2S, and changes in the oxidation state of the ore fluid. Effervescence of CO_2 causes a sharp increase in pH, which in turn destabilizes the tungsten and precious metal-bearing complexes. This suggests that the deposition of scheelite, Au-Ag tellurides and native precious metals and electrum was due to phase separation related to CO_2-effervescence. The escape of volatiles neutralized the pH of the mineralizing fluid from 3.3 at 400°C to 4.6 at 300°C, 5.7 at 250°C and 6.5 at 200°C for the Panormos Bay ores and from 6.9 at 200°C to 7.6 at 150°C at Apigania Bay (Tombros, 2001). In conclusion, W, Au-Ag-Te and Au-Ag ore deposition was predominantly controlled by gaseous phase separation, which resulted in pH neutralization.

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